Patent
Docket No. 58399US002

PATTERNED COATING METHOD

Field of the Invention

[0001] This invention relates to methods for forming patterned coatings.

Background

[0002] In many applications, especially those involving electronics, patterned coatings must be formed in one or more layers on a substrate. Available pattern formation methods include masking the substrate with tape and photoimaging. In masking, a tape is applied in a pattern over parts of the substrate. After coating the substrate using any convenient method (e.g., spin coating) and drying or curing the coating, the tape can be manually removed, leaving the patterned coating. However, coating build-up or edge distortion sometimes occurs near the pattern boundaries, and applying and removing the tape can be tedious. In photoimaging, a photocurable polymer is applied to the substrate, imaged in a pattern (using, for example a partially transparent and partially occluded mask and UV or shorter wavelength light), then removed from the unimaged areas (in a step sometimes called "lift-off") using a suitable solvent. The choice of suitable photoimaging resins may be somewhat limited because many removal solvents may adversely affect the photocured polymer coating. The removal solvent may also pose environmental and other hazards.

[0003] References describing patterned coating or printed circuit formation include U.S. Patent Nos. 3,931,454, 5,121,134, 5,145,717 5,165,962, 5,658,469, 5,759,625, 6,300,042 B1, 6,329,227 B2, 6,498,114 B1 and 6,559,474 B1. U.S. Patent No. 5,468,324 describes a method for data recording duplication and microstructure fabrication. U.S. Patent No. 6,352,758 B1 describes a patterned article. References involving masking include U.S. Patent Nos. 5,104,711 and 5,165,962.

Summary of the Invention

[0004] The present invention provides, in one aspect, a method for preparing a patterned article comprising:

a) applying a release polymer to a portion of a substrate in a desired pattern;

b) applying a substrate-adherent polymer over the pattern and over at least a portion of the substrate in a continuous layer having a substantially constant height with respect to the substrate; and

c) mechanically removing the substrate-adherent polymer from the pattern.

[0005] The invention provides, in another aspect, a method for preparing a patterned article comprising:

a) applying a release polymer to a portion of a substrate in a desired pattern;

b) applying a continuous layer of a substrate-adherent polymer over the pattern and over at least a portion of the substrate;

c) applying an adhesive tape to the substrate-adherent polymer; and

d) removing the adhesive tape and substrate-adherent polymer adhered to the tape while leaving a portion of the substrate-adherent polymer adhered to the substrate in a negative of the pattern.

[0006] The invention provides, in a further aspect, a method for preparing a patterned article comprising:

a) applying a submicron-thickness release polymer layer to a portion of a substrate in a desired pattern;

b) applying a continuous submicron-thickness polyimide layer over the pattern and over at least a portion of the substrate; and

c) removing a portion of the polyimide layer from the release polymer while leaving the remainder of the polyimide layer adhered to the substrate in a negative of the pattern.

Brief Description of the Drawing

[0007] **Fig. 1** is a cross-sectional view of a substrate partially coated with a release polymer.

[0008] **Fig. 2** is a cross-sectional view of the article of **Fig. 1** overcoated with a substrate-adherent polymer.

[0009] **Fig. 3** is a cross-sectional view of the article of **Fig. 2** covered with an adhesive tape.

[0010] **Fig. 4** is a cross-sectional view of the article of **Fig. 3** as the adhesive tape is being peeled away.

[0011] **Fig. 5** is a cross-sectional view of the article of **Fig. 3** after the adhesive tape has been peeled away.

[0012] **Fig. 6** is a cross-sectional view of an impact media technique for mechanically removing a portion of the substrate-adherent polymer from the release polymer.

[0013] **Fig.** 7 through **Fig. 11** are profilometer graphs.

Detailed Description

[0014] By using the term "polymer" we refer to homopolymers and copolymers, as well as to homopolymers or copolymers that may be formed in a miscible blend, e.g., by coextrusion or by reaction, including, e.g., transesterification. The term "copolymer" includes both random and block copolymers.

[0015] By using the term "film former" we refer to a material that can be coated in a thin film (e.g., of about 0.05 mm) on a suitable substrate to form a substantially continuous coating.

[0016] By using words of orientation such as "atop", "on", "uppermost" and the like for the location of various elements in an article, we refer to the relative position of the element with respect to a horizontal support or reference plane. We do not intend that such elements or articles should have any particular orientation in space during or after their manufacture.

[0017] By using the term "overcoated" to describe the position of a layer with respect to a substrate or other element (e.g., an underlying layer) in an article, we refer to the recited overcoated layer as being atop the substrate or other element, but not necessarily contiguous to the substrate or other element. By using the term "separated by" to describe the position of a first element with respect to two other elements, we refer to the first element as being between the other elements but not necessarily contiguous to either other element.

[0018] By using the term "surface energy" with respect to a polymer, we refer to the measured surface energy of a thin film of the polymer determined using a contact angle goniometer and two test liquids as described in D. K. Owens and R. C. Wendt, *J. Appl Polym. Sci.* 13, 1741 (1969).

[0019] By using the term "mechanically removing" with respect to a polymer layer, we refer to removal methods that rely on adhesion to, abrasion of or physical impact (including impact from a jet of air, water or a solution containing water) upon the polymer layer and that do not require (but can if desired be augmented by) the application of an organic solvent to the polymer layer.

[0020] Referring to **Fig. 1**, patterned article **10** has glass substrate **12** overcoated on a portion of its upper surface **13** with release polymer **14**. Release polymer **14** forms a pattern (not shown in **Fig. 1**) on upper surface **13** representing, for example, circuit traces, electrical

connections, electrodes or the like. The upper surface **15** of release polymer **14** preferably has a lower surface energy than upper surface **13**.

[0021] **Fig. 2** illustrates an intermediate article **20** made by applying substrate-adherent polymer **22** atop patterned article **10**. Substrate-adherent polymer **22** forms a continuous layer atop release polymer **14** having a substantially constant height **h** with respect to substrate **12**. Release polymer **14** preferably has a sufficiently low surface energy so that substrate-adherent polymer **22** forms at best a weak bond to release polymer **14** that can readily be debonded using mechanical measures described in more detail below. Substrate-adherent polymer **22** has greater adhesion to substrate **12** than to release polymer **14**.

[0022] **Fig. 3** illustrates an intermediate article **30** made by attaching adhesive tape **32** atop article **20**. Adhesive tape **32** has backing **34** and adhesive layer **36**. Substrate-adherent polymer **22** has greater adhesion to adhesive layer **36** than to release polymer **14**, but has lower adhesion to adhesive layer **36** than to substrate **12**.

[0023] **Fig. 4** illustrates one method for mechanically removing substrate-adherent polymer **22** from the pattern atop substrate **12**. As shown by the arrow in **Fig. 4**, tape **32** can be peeled away from substrate **12** to remove substrate-adherent polymer **42** adhered to tape **32** while leaving substrate-adherent polymer **22** adhered to substrate **12** in a negative of the pattern or "pattern negative". This step provides patterned article **40** whose upper surface is covered with a pattern formed by regions covered with release polymer **14** and a pattern negative formed by regions covered with substrate-adherent polymer **22**.

[0024] **Fig. 5** illustrates a patterned article **50** that can be made by washing away release polymer **14** using a suitable solvent. This washing step is optional and will not be needed or desired in all applications. The upper surface of article **50** has a pattern formed by exposed, uncovered regions (formerly covered by release polymer **14**) and a pattern negative formed by regions covered with substrate-adherent polymer **22**.

[0025] **Fig. 6** illustrates another method for mechanically removing substrate-adherent polymer **22** from the pattern atop substrate **12**. This method can be carried out using article **20** shown in **Fig. 2**. Impact media **62** propelled through orifice **64** in impact abrading device **66** abrade away the portion of substrate-adherent polymer **22** atop release polymer **14**. If desired, further application of impact media **62** can be used to abrade away release polymer **14** as well.

[0026] A variety of substrates can be employed in the invention. Suitable substrates include but are not limited to inorganic substrates such as quartz, glass, silica and other oxides or ceramics such as alumina, indium tin oxide, lithium tantalate ($LiTaO_3$), lithium niobate

($LiNbO_3$), gallium arsenide (GaAs), silicon carbide (SiC), langasite (LGS), zinc oxide (ZnO), aluminum nitride (AlN), silicon (Si), silicon nitride (Si_3N_4), and lead zirconium titanate ("PZT"); metals or alloys such as aluminum, copper, gold, silver and steel; thermoplastics such as polyesters (e.g., polyethylene terephthalate or polyethylene naphthalates), polyacrylates (e.g., polymethyl methacrylate or "PMMA"), poly(vinyl acetate) ("PVAC"), poly(vinylbutyral) ("PVB)", poly(ethyl acrylate) ("PEA"), poly(diphenoxyphosphazene) ("PDPP"), polycarbonate ("PC"), polypropylene ("PP"), high density polyethylene ("HDPE"), low density polyethylene ("LDPE"), polysulfone ("PS"), polyether sulfone ("PES"), polyurethane ("PUR"), polyamide ("PA"), polyvinyl chloride ("PVC"), polyvinylidene fluoride ("PVdF"), polystyrene and polyethylene sulfide; and thermoset plastics such as cellulose derivatives, polyimide, polyimide benzoxazole and polybenzoxazole. Preferably care is taken when selecting the substrate so that there will be an adequate degree of adhesion between the substrate and the substrate-adherent polymer. If desired, the substrate can be washed with a suitable solvent to enhance adhesion of the release polymer or substrate-adherent polymer or both. The substrate can instead or in addition to be pretreated to enhance such adhesion. Preferred pretreatments include but are not limited to electrical discharge in the presence of a suitable reactive or non-reactive atmosphere (e.g., plasma, glow discharge, corona discharge, dielectric barrier discharge or atmospheric pressure discharge); chemical pretreatment (e.g., with a low solids solution of polyvinylidene dichloride or with a solvent-borne mixture of a polyester resin and an aziridine crosslinker); flame pretreatment; ultraviolet light pretreatment with or without ozone pretreatment; and incorporating functional polymers into the substrate when a polymeric substrate is employed.

[0027] A variety of release polymers can be employed. Preferred release polymers include but are not limited to silicone polymers, fluorochemical polymers and polymers containing long alkyl side chains. Suitable silicone polymers include silicone polyurethanes, silicone polyureas, silicone polyurethane/ureas and silicone acrylate grafted copolymers such as those described in U.S. Patent Nos. 4,728,571, 5,032,460, 5,202,190, 5,214,119, 5,290,615, 5,356,706 and 5,750,630. Suitable fluorochemical-containing polymers include those described in U.S. Patent No. 3,318,852. Suitable polymers containing long alkyl side chains include polyvinyl N-alkyl carbamates such as polyvinyl N-octadecyl carbamates, and copolymers containing higher alkyl acrylates or methacrylates such as octadecyl acrylate, stearyl methacrylate or behenyl acrylate, e.g., those described in U.S. Patent Nos. 2,532,011, 2,607,711, 3,502,497 and 4,241,198. In polymers containing long alkyl side chains, the side chain preferably includes from about 16 to 22 carbon atoms. The release polymer can include additives such as fillers, pigments, wetting

agents, viscosity modifiers, stabilizers, anti-oxidants or cross-linking agents. The release polymer can be formed *in situ*, or applied as a preformed polymer carried in a suitable solvent. The release polymer can be crosslinked if desired. As noted above, the release polymer preferably has a sufficiently low surface energy so that the substrate-adherent polymer forms at best a weak bond to the release polymer. This does not require that the release polymer have a lower surface energy than the substrate-adherent polymer. A variety of factors other than surface energy may govern the degree of adhesion between the release polymer and the substrate-adherent polymer, including the respective chemical compositions of the release polymer and substrate-adherent polymer and their respective surface topologies. Preferably however the release polymer has a surface energy less than that of the substrate-adherent polymer. The release polymer preferably is a film former that can be applied to form a coating that when dried or cured will have a thickness below about 3 μm, more preferably below about 2 μm, and for some applications a preferred submicron thickness. A variety of coating techniques can be employed to apply the release polymer, including swabbing, dip coating, roll coating, spin coating, spray coating, die coating, ink jet coating, screen printing (e.g., rotary screen printing), gravure printing and flexographic printing. If the release polymer is formed *in situ*, a variety of techniques can be employed to form the release polymer including exposure to heat, UV, electron beam or laser energy; two-part chemical cure systems; one part chemical cure systems that are prevented from premature cure by the use of a suitable blocking agent or encapsulants; and other techniques that will be familiar to those skilled in the art.

[0028] A variety of substrate-adherent polymers can be employed. Preferred substrate-adherent polymers include but are not limited to PMMA, PVAC, PVB, PEA, PDPP, fluoropolymers, epoxies, polyhexamethyldisiloxane ("HMDSO"), polyimides and polystyrene. The substrate-adherent polymer can include additives such as fillers, pigments, wetting agents, viscosity modifiers, stabilizers, anti-oxidants or cross-linking agents. The substrate-adherent polymer can be formed in situ, or applied as a preformed polymer carried in a suitable solvent. The substrate-adherent polymer can be crosslinked if desired. Preferably the substrate-adherent polymer has a surface energy greater than that of the release polymer. As a general guide, the substrate-adherent polymer preferably also has a surface energy greater than that of the substrate. If desired, the substrate-adherent polymer can include various adjuvants such as small particle fillers, surface active agents, UV absorbers, photoinitiators, colorants and indicators. The substrate-adherent polymer preferably is applied at a thickness greater than that of the release polymer but not so great as to make it difficult to remove the substrate-adherent polymer

from the pattern. As a general guide, the substrate-adherent polymer thickness preferably is about 2 to about 10 times the release polymer thickness, and more preferably about 3 to about 7 times the release polymer thickness. As a further general guide, the substrate-adherent polymer preferably is a film former that can be applied to form a coating that when dried or cured will have a thickness with respect to the substrate of about 3 μm to about 15 μm, more preferably about 3 to about 10 μm, and most preferably about 3 to about 5 μm.

[0029] The substrate-adherent polymer is applied in a continuous layer over the pattern. This preferably provides a smooth, continuous substrate-adherent polymer coating having a substantially constant height with respect to the substrate. If the substrate-adherent polymer coating is not sufficiently thick to cover the release polymer pattern then it will not provide a continuous layer over the release polymer pattern having a substantially constant height with respect to the substrate and the eventual edges or margins of the pattern negative may be uneven or otherwise inadequately defined, or the pattern may exhibit edge artifacts.

[0030] A variety of coating techniques can be employed to apply the substrate-adherent polymer including those mentioned above with respect to the release polymer. If the substrate-adherent polymer is formed *in situ*, a variety of polymerization techniques can be employed including those mentioned above with respect to the release polymer.

[0031] The substrate-adherent polymer can be removed from the pattern using a variety of mechanical methods. Suitable mechanical removal methods include but are not limited to the use of adhesive tape or impact media as described above, as well as the use of low impact or high impact coating dislodgment aids such as sandpaper, buffing pads, pressurized air and ultrasonic horns. Mechanical removal may facilitate the formation of a pattern having sharply defined edges. Following removal of the substrate-adherent polymer, the release polymer can be left atop the substrate or if desired can also be removed, thereby exposing a portion of the substrate. A variety of removal techniques can be employed, including but not limited to the use of solvents or impact media as described above, as well as the use of other coating dislodgement aids such as those just described for removal of the substrate-adherent polymer. When a solvent is employed, the solvent selection will depend in part upon the chosen release polymer. For fluoropolymers, hydrofluoroethers are particularly preferred removal solvents.

[0032] The invention can be used to make a variety of patterned articles including printed circuit boards, electrical connectors, information displays, electronic components, passivation layers and dielectric layers.

[0033] The invention is further illustrated in the following illustrative examples, in which all parts and percentages are by weight unless otherwise indicated.

Example 1

[0034] Using a hand-held cotton swab, generally C-shaped and generally straight streaks of FLUORAD™ FC-722 fluoroaliphatic copolymer coating (formerly commercially available from Dyneon LLC Oakdale, MN) were formed on the surface of a 50 mm X 75 glass slide. A rapid application rate was employed in order to obtain a release polymer coating thickness of about 0.1 μm as measured using a TENCOR™ profilometer (commercially available from KLA-Tencor Corporation, San Jose, CA). **Fig. 7** shows the profilometer scan. In cross-section the release polymer coating looked like coating **14** in **Fig. 1**.

[0035] Using a spin-coating apparatus operated at 6000 rpm, No. PI 2579B polyimide (commercially available from HD Microsystems LLC, Parlin, N.J.) was coated over the pattern and over the remainder of the substrate to form a substrate-adherent polymer coating having a substantially constant height of about 0.3 μm with respect to the substrate. In cross-section the resulting article looked like article **20** in **Fig. 2**. A piece of Scotch Transparent Tape 600 (commercially available from 3M Company, St. Paul, MN) was placed atop the polyimide coating over the pattern and pressed into place to form an article which in cross-section looked like article **30** in **Fig. 3**. The tape was peeled away from the substrate as shown in **Fig. 4**, thereby removing the substrate-adherent polymer from atop the release polymer pattern and forming a patterned article which in cross-section looked like article **40** in **Fig. 4**. **Fig. 8** shows a profilometer scan of the patterned article. As shown in **Fig. 8**, the edges of the pattern negative were sharply defined with the major exposed portion of each sidewall being generally perpendicular to the substrate, and both the release polymer nominal coating thickness and the substrate-adherent polymer nominal coating thickness were generally unchanged near the boundary between the release polymer and substrate-adherent polymer.

[0036] The fluoropolymer layer was removed from the patterned article by rinsing with NOVEC™ Engineered Fluid HFE-7200 hydrofluoroether (commercially available from 3M Company, St. Paul, MN) to form a patterned article which in cross-section looked like article **50** in **Fig. 5**. **Fig. 9** shows a profilometer scan of the patterned article. The edges of the pattern negative remained sharply defined with the major exposed portion of each sidewall remaining generally perpendicular to the substrate.

Example 2

[0037] Using the general method of Example 1, a fluoropolymer release polymer pattern was formed on a glass slide. The release polymer was overcoated with a solvent-based ink applied by dip coating to form a 0.5 μm thick substrate-adherent polymer coating. A portion of the substrate-adherent polymer was removed using tape, and the underlying release polymer was removed using HFE-7200 hydrofluoroether. **Fig. 10** and **Fig. 11** show profilometer scans of the patterned article before and after removal of the release polymer. As shown in **Fig. 10** and **Fig. 11**, the substrate-adherent polymer edges were sharply defined with the major exposed portion of each sidewall being generally perpendicular to the substrate.

[0038] Various modifications and alterations of this invention will be apparent to those skilled in the art without departing from the scope and spirit of this invention. This invention should not be restricted to that which has been set forth herein only for illustrative purposes.